

CONVERSION OF METHANE TO HIGHER HYDROCARBONS  
BY SUPPORTED ORGANOMETALLIC COMPLEXES

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ABSTRACT

Novel highly dispersed metal catalysts were prepared by attaching metal clusters to inorganic oxides. The hydridoruthenium complexes (containing one, four or six ruthenium atoms) were first reacted with triethylaluminum, which releases one equivalent of ethane per hydride to give a novel aluminum-containing complex. These complexes were then anchored to the support (alumina, zeolite 5A, or Y-zeolite) by reaction with acidic sites, in which another equivalent of ethane was released. These catalysts were active in the conversion of methane to  $C_2$  and higher hydrocarbons at 750°C using a fixed-bed down-flow reactor under anaerobic condition. Up to 50% selectivity for higher hydrocarbons was observed with the alumina supported hexameric ruthenium clusters. The zeolite supported tetrameric cluster produced less coke than the other catalysts apparently due to the cluster being located inside the zeolite supercage.

INTRODUCTION

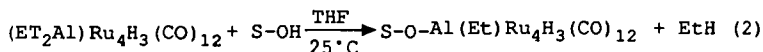
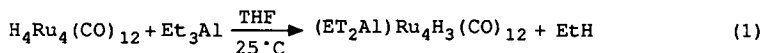
Research on the technique of surface confinement to produce novel catalysts for a wide variety of processes is continuing in many laboratories.<sup>1-4</sup> We have been working on the development of novel catalysts for converting methane to higher hydrocarbons. The catalysts are prepared by reacting organometallic complexes of transition metals with inorganic oxide supports to produce surface-confined metal complexes.<sup>5</sup> The metal complex is then decomposed to obtain very stable, highly dispersed catalysts. The increased activity of highly dispersed catalysts is desirable for activating the relatively inert methane and because highly dispersed catalysts are resistant to coking. The use of zeolitic supports will stabilize the highly dispersed catalysts which are confined inside the zeolite pores. The variables we studied include cluster size, supporting materials, and reaction conditions.

## EXPERIMENTAL DETAILS

### Synthesis of catalysts

The synthesis of these catalysts involves three steps. The first step is to synthesize the ruthenium cluster precursors. The second step is a novel approach developed in our laboratory that involves the reaction of the organometallic clusters with alkyl aluminum. The final step is to anchor these catalysts on supports by a chemical reaction between the hydroxy group of the support and the alkyl groups of the organometallic cluster to give a covalent chemical bond.

The organometallic complexes include a monoruthenium complex,  $\text{Ru(allyl)}_2(\text{CO})_2$ ; a tetrameric ruthenium cluster,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ ; a hexameric ruthenium cluster,  $\text{H}_2\text{Ru}_6(\text{CO})_{18}$ ; and a mixed metal cluster,  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ ; all were prepared according to literature procedures.<sup>6,7</sup> The hydrido clusters reacted with triethyl aluminum at room temperature (eq. 1). The reaction stoichiometries were determined by measuring the quantity of ethane produced.<sup>5</sup> These alkyl aluminum carbonyl ruthenium clusters were then used to react with acidic supports: -alumina, 5A molecular sieves, and LZ-Y 52 zeolite. The reaction stoichiometries were again determined by measuring the quantity of ethane produced (eq. 2).



The monomeric ruthenium complex reacted directly with the acidic support to release one equivalent of propylene. The tetraruthenium and the mixed iron-ruthenium clusters were also supported on magnesium oxide by the reaction of acidic hydride with the basic oxide. All support materials were in powder form except for the 5A molecular sieves which was 60-80 mesh.

### General Procedure for testing catalysts

The activity of the catalysts were tested using a conventional fixed-bed down-flow reactor. In a typical run, the catalyst (0.5 g) was loaded into a stainless steel reactor (0.22 inch ID) under an inert atmosphere. The reactor was connected to the reactor system and purged with helium for 15 min. A helium diluted methane gas (contains 20% methane) was introduced through a mass flow controller to the reactor. A back pressure regulator was set at 50 psig and the methane flow rate was controlled by the mass flow controller. A thermocouple was immersed in the catalyst bed and connected to a temperature controller. The outlet gases were fed to a Carle 500 gas chromatography for sample analysis. The GC was programmed to separate light gases including hydrogen and hydrocarbons up to  $C_5$ . The  $C_6$  and higher hydrocarbons and other polar compounds ( $C_6+$ ) were back flushed from the column to the detector. The calibration of  $C_6+$  was based on the area integration and referenced to the methane peak. Other components were calibrated with standard sample mixtures. Initial methane concentration was measured before and after each run at ambient temperature under the same conditions. Each sample run lasted for at least 15 h and the products were analyzed every hour. During the first 2 h of the reactions, we detected small amounts of CO, which was released from the decomposition of the metal complexes. The analytical data from the first 3 h of reactions were discarded and the subsequent 12 h data were averaged.

### RESULTS AND DISCUSSION

The ruthenium catalysts were tested at 750°C under 50 psig pressure. Three different sizes of ruthenium clusters: monomer (Ru), tetramer ( $Ru_4$ ), and hexamer ( $Ru_6$ ) were supported on three different supports:  $\gamma$ -alumina, 5A molecular sieve, and Y-zeolite. The results are summarized in Table 1. We used a commercial ruthenium catalyst which is supported on alumina (obtained from Engelhard) for comparison. The amount of metal loading were based on elemental analyses (Galbraith Laboratory).

### Effects of cluster size

The commercial ruthenium catalyst gave a very high conversion of methane (71.2%) but no hydrocarbon product was detected. Methane conversion on the monoruthenium catalysts were considerably lower than the ruthenium clusters ( $\text{Ru}_4$  and  $\text{Ru}_6$ ). In general, methane conversions depend on the type of support and decreased in the order of alumina, 5A molecular sieve, and zeolite. These results suggested that the methane conversion was related to the amount of surface bonded metal. On alumina, the metals are located on the surface while on 5A molecular sieves and on zeolite, increased amount of metal were located inside the zeolite pore. The differences of methane conversions were more obvious for the  $\text{Ru}_4$  catalyst where the conversion decreased from 10.1 to 4.9 and to 1.7% on alumina, 5A molecular sieve, and Y-zeolite, respectively.

Our intention in using different supports is to confine the ruthenium cluster at different locations on or within the support. Hence, the  $\text{Ru}_4$  and  $\text{Ru}_6$  clusters are dispersed on the alumina surface but are partly confined inside the pores of zeolite supports. The pore size of 5A molecular sieve is too small for the  $\text{Ru}_6$  cluster but should be large enough for the  $\text{Ru}_4$  cluster after decomposition. Since the Y-zeolite has the largest pore ( $\sim 17$ ), most of the  $\text{Ru}_4$  are located inside the zeolite pore.

### Product selectivity

All the ruthenium catalysts producedthane and ethylene. The selectivity of  $\text{C}_2$  hydrocarbons for  $\text{Ru}_4$  clusters increased as the percent conversion of methane decreased. The  $\text{Ru}_6\text{AL}$  has the highest total hydrocarbon yield which probably due to the higher metal loading. The total hydrocarbon yield on  $\text{Ru}_6\text{MS}$  and  $\text{Ru}_6\text{ZL}$  are about the same but the  $\text{Ru}_6\text{ZL}$  has a higher selectivity for  $\text{C}_2$  product. Confining the metal cluster inside the zeolite cage may also limite the propagation of methane polymerization. The ruthenium monomers gave relatively low hydrocarbon yields indicating that polymerization of methane required more than one metal atom.

Table 1

ACTIVITY OF RUTHENIUM CATALYSTS ON METHANE DEHYDROGENATION<sup>a</sup>

Catalyst <sup>b</sup>	Ru(wt%)	Flow Rate (mL/min)	Methane Conver(%)	Selectivity <sup>c</sup> to		
				H <sub>2</sub> (%)	C <sub>2</sub> (%)	C <sub>6+</sub> (%)
Ru-com	0.50	50	71.2	151.0	-- <sup>d</sup>	--
RuAL	0.35	10	3.0	139.9	2.8	--
RuMS	0.31	10	2.3	147.5	1.2	--
RuZL	0.37	10	1.7	177.5	2.6	--
Ru <sub>4</sub> AL	0.61	100	10.1	78.6	1.62	--
Ru <sub>4</sub> MS	0.49	100	4.9	146.6	3.52	--
Ru <sub>4</sub> ZL	0.61	50	1.7	25.3	6.9	28.9
Ru <sub>6</sub> AL	1.26	50	6.1	113.4	6.9	41.4
Ru <sub>6</sub> MS	0.19	50	5.6	192.8	1.0	14.8
Ru <sub>6</sub> ZL	0.20	50	3.6	161.9	3.6	10.0

<sup>a</sup>Reaction condition: temperature=750C, pressure=150 psig.

<sup>b</sup>Abbreviation: Ru-com=commercial ruthenium catalyst from Engelhard;  
 Ru<sub>4</sub>=(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlRu<sub>4</sub>H<sub>3</sub>(CO)<sub>12</sub>; Ru<sub>6</sub>=(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlRu<sub>6</sub>H(CO)<sub>18</sub>;

Ru=Ru(Allyl)(CO)<sub>2</sub>; AL--alumina; MS=5A molecular sieve; ZL=LZ-Y-zeolite.

<sup>c</sup>Selectivities were calculated on converted methane. Selectivity to hydrocarbons are based on carbon number.

<sup>d</sup>Not detected.

Coking

The results listed in Table 1 show that more than one equivalent of hydrogen was produced per methane input, which suggests that some of the methane turned to coke. The elemental analyses listed in Table 2 showed that the Ru<sub>4</sub>AL, Ru<sub>4</sub>MS, Ru<sub>6</sub>AL and Ru<sub>6</sub>MS contained more carbon after reaction with methane. In contrast, the carbon content of the Ru<sub>4</sub>ZL decreased after reaction. Thus, those catalysts having metal dispersed on the support surface (and therefore larger particle size) promote coke formation while the metals confined inside the zeolite cages have much reduced coking. For the Ru<sub>4</sub>MS, the carbon content only increased slightly to 4.38% as compared to more than 20% for the Ru<sub>4</sub>AL suggesting that at least a portion of the metal clusters are located inside the

cages of the molecular sieve. On Y-zeolite, the  $\text{Ru}_4$  cluster in fact showed a decrease in carbon content indicating very low coking. The decrease is due to the decomposition of the ruthenium complexes, i.e. release of carbon monoxide.

Table 2

ELEMENTAL ANALYSES OF RUTHENIUM CATALYSIS FOR METHANE DEHYDROGENATION<sup>A</sup>

Catalyst	Before Reaction			After Reaction		
	%C	%H	%Ru	%C	%H	%Ru
$\text{Ru}_4\text{AL}$	5.09	1.04	0.61	26.50	0.40	0.57
$\text{Ru}_4\text{MS}$	1.46	1.13	0.49	4.38	0.46	0.64
$\text{Ru}_4\text{ZL}$	5.25	1.53	0.61	0.58	0.22	1.26
$\text{Ru}_6\text{AL}$	9.77	1.84	1.26	23.24	0.67	0.55
$\text{Ru}_6\text{MS}$	0.95	1.68	0.19	22.29	0.19	0.32

<sup>a</sup>Reaction with methane at 750C for 15 h.

Effect of reaction conditions

The effect of reaction temperature is similar for every catalyst. Higher methane conversion and product yield are obtained at higher temperature. These results are expected because polymerization of methane is thermodynamically unfavored process.<sup>8</sup> Increasing the reaction pressure has a similar effect on the methane conversion. However, the product selectivities for hydrogen and C2 hydrocarbons decrease but increases for C6+ hydrocarbons (Table 3). Highest selectivity is observed at 150 psig. As expected, increasing the space velocity lowers the methane conversion but increase the selectivity of hydrocarbon products.

Basic support and mixed metal cluster

Methane conversion on the magnesia supported ruthenium monomer and the  $\text{FeRu}_3$  cluster are much higher than the zeolite supported analogs (Table 4). However, the product selectivities to hydrocarbons are lower.

Table 3

EFFECT OF REACTION PRESURE AND SPACE VELOCITY TO  
THE ACTIVITY OF  $\text{Ru}_6\text{ZL}^a$  AT  $750^\circ\text{C}$

Pressure (psig)	Flow rate mL/min	%CH <sub>4</sub> Conversion	%Selectivity <sup>b</sup> of		
			H <sub>2</sub>	C <sub>2</sub>	C <sub>6+</sub>
50	50	3.18	164.16	6.04	6.6
150	50	5.19	91.33	4.48	10.70
250	50	8.64	82.41	2.46	7.38
250	100	2.62	177.10	9.24	20.64

<sup>a</sup> $\text{Ru}_6\text{ZL}$  - zeolite supported  $\text{Ru}_6$  cluster,  $\text{C}_2\text{H}_5\text{AlRu}_6\text{H}(\text{CO})_{18}$ .

<sup>b</sup>Selectivity was based on carbon number of hydrocarbon and the amount of methane reacted.

Table 4

CATALYTIC REACTIVITY OF ZEOLITE AND MAGNESIA  
SUPPORTED CATALYSTS FOR METHANE DEHYDROGENATION<sup>a</sup>

Catalysts	Temp( $^\circ\text{C}$ )	Methane Conversion(%)	Selectivity <sup>b</sup>	
			C <sub>2</sub> (%)	C <sub>6+</sub> (%)
$\text{RuMgO}$	600	21.044	0.1	0.5
$\text{Ru}_4\text{MgO}$	750	4.04	6.9	49.2
$\text{FeRu}_3\text{ZL}$	600	3.07	1.9	18.5
$\text{FeRu}_3\text{MgO}$	600	8.87	0.1	--

<sup>a</sup>Reaction conditions: pressure=150psig, flow rate=20 mL/min, weight of catalyst=2 g, reactor O.D.-3/8in (S.S.).

<sup>b</sup>Selectivity to hydrocarbon is based on carbon number.

<sup>c</sup>Not detected.

For the mixed iron-ruthenium catalysts, magnesia support also increased the methane conversion. At  $600^\circ\text{C}$ , the methane conversion was 8.87% for  $\text{FeRu}_3\text{MgO}$  and was 3.07% for  $\text{FeRu}_3\text{ZL}$ . At  $750^\circ\text{C}$ , methane conversion increased to 41.5% and 23.05% for  $\text{FeRu}_3\text{MgO}$  and  $\text{FeRu}_3\text{ZL}$ , respectively. These catalysts behave similarly to the ruthenium monomers in that the hydrocarbon yields were lower on the magnesia supported catalyst.

Increased temperature has a similar effect on the methane conversion over  $\text{FeRu}_3\text{ZL}$ , but the methane conversion was lower than the  $\text{MgO}$  supported catalysts. At  $750^\circ\text{C}$ , the methane conversion was 23.05%. Hydrocarbon yields increased as the reaction temperature increased from  $500^\circ$  to  $600^\circ\text{C}$  and then declined at higher temperature. The maximum yield of  $\text{C}_2$  was 0.06% of the input methane and was 0.57% for  $\text{C}_6+$ . Since the  $\text{Ru}_4\text{ZL}$  was essentially not active at  $600^\circ\text{C}$ , this low temperature reactivity of  $\text{FeRu}_3\text{ZL}$  is obviously due to an effect of the mixed metal. Introduction of the iron to the metal cluster is advantageous to methane dehydrogenation activity. Figure 3 shows the effect of increasing temperature on methane conversion and on hydrocarbon yield. Highest hydrocarbon yield was obtained at  $600^\circ\text{C}$ . However, the hydrogen selectivity was 170% at this temperature which suggests coke formation.

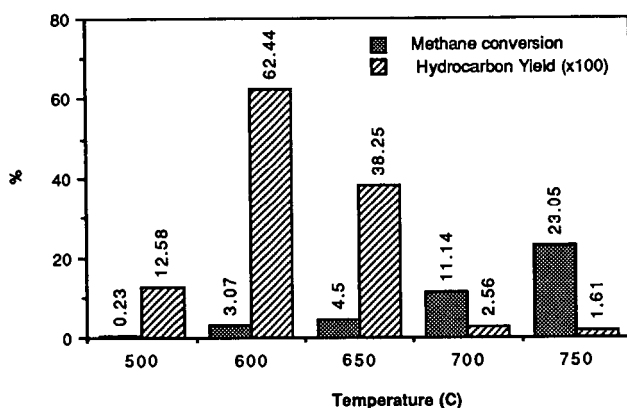


Figure 1. Activity of  $\text{FeRu}_3\text{ZL}$  for methane reforming at various temperatures.

#### CONCLUSION

Most of the reports on catalytic conversion of methane to higher hydrocarbons are based on metal oxides by the oxidative coupling pathway. Few examples have been reported of direct methane dehydrogenation. Table 5 lists some of the literature results on both oxidative coupling and dehydrogenation together with our results.



It is difficult to truly compare the catalytic activities of the catalysts because the experimental condition are so different. However, based on the methane conversion and the selectivities of higher hydrocarbons, our catalysts are comparable. Interestingly, we have not detected any mid-ranged hydrocarbons ( $C_3$ - $C_5$ ). Mitchell and Waghorne reported the major product of alumina supported CaCrPt catalyst under anaerobic condition was benzene.<sup>9</sup> Jones et al. also observed small amounts of benzene produced from methane dehydrogenation over silica support  $GeO_2$ .<sup>10</sup> We have not yet identified our  $C_{6+}$  product, but it is possible that it contains benzene.

Table 5

COMPARISON OF THE ACTIVITIES OF CATALYSTS FOR METHANE DEHYDROGENATION

Catalyst	$CH_4/O_2$	Temp. (°C)	Press (atm)	GHSV ( $h^{-1}$ )	$CH_4$ conv(%)	Selectivity to	
						$C_2$	$C_6$
Li/MgO <sup>a</sup>	2	720	1	2754	37.8	50.3	N.R. <sup>h</sup>
CaCrPt/AL <sup>b</sup>	>200 <sup>j</sup>	705	1	N.R.	27.64 <sup>i</sup>	31.4	68.3
PbO/MgO <sup>c</sup>	6	750	1	8000	10.0	65.5	N.R.
Sm <sub>2</sub> O <sub>3</sub> <sup>d</sup>	6	750	1	$3.8 \times 10^7$	6.5	60.0	N.R.
Sb <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> <sup>e</sup>	>200	800	1	600	0.25 <sup>i</sup>	82.9	N.R.
GeO <sub>2</sub> /SiO <sub>2</sub> <sup>f</sup>	>200	700	1	860	0.22	57.1	3.3 <sup>k</sup>
Ru <sub>6</sub> AL <sup>g</sup>	>200	750	4.5	16000	6.06	6.9	41.4
Ru <sub>4</sub> ZL <sup>g</sup>	>200	750	4.5	16000	1.74	6.9	28.9
Ru <sub>4</sub> MgO <sup>g</sup>	>200	750	4.5	6200	4.04	6.9	49.2
FeRu <sub>3</sub> ZL <sup>g</sup>	>200	600	4.5	6200	3.07	1.9	18.5

<sup>a</sup>T. Ito; J-X Wang; C-H, Lin; J.H. Lunsford, J. Am. Chem. Soc., 107, 5062 (1986).

<sup>b</sup>H.L. Mitchell, III; R.H. Waghorne; U.S. Patent No. 4239658 (1980).

<sup>c</sup>K. Asami; S. Hashimoto; T. Shikada; Chem. Letter 1233 (1986).

<sup>d</sup>K. Otsuka, T. Komatsu; Chem. Lett. 483 (1987).

<sup>e</sup>C.A. Jones, J.J. Leonard; J.A. Sofranko; U.S. Patent 4,443,644 (1984).

<sup>f</sup>C.A. Jones, J.J. Leonard; J.A. Sofranko; U.S. Patent 4,554,395 (1985).

<sup>g</sup>This work.

<sup>h</sup>Not reported.

<sup>i</sup>Cumulative result.

<sup>j</sup>No oxygen added.

<sup>k</sup>benzene.

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